Diheterocyclic Compounds from Dithiocarbamates and Derivatives Thereof. II [1]. 2,2'-Diamino-6,6'-Bibenzoazoles

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The readily available dithiocarbamates and dithiocarbonimidates **4**, **8**, **14** and **15** afford in one step the title compounds in medium to very good yields. In each case, the choice of reagent depends on the nature of the group to be introduced. Their usefulness as synthetic equivalents of weakly reactive or unavailable isothiocyanates is also discussed.

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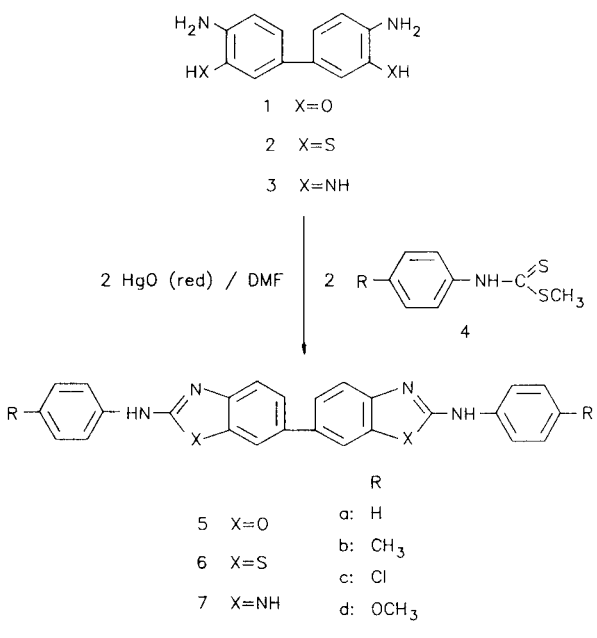
We have previously reported the versatility of dithiocarbamates [2] and related compounds in heterocyclic synthesis. In this paper we wish to report a general approach to the synthesis of symetrically-substituted 6,6'-bibenzoazoles, which makes use of the reactivity of dithiocarbamic and dithiocarbonimidic acid esters derived from arylamines [3], hetarylamines [4] and arenesulfonamides [5].

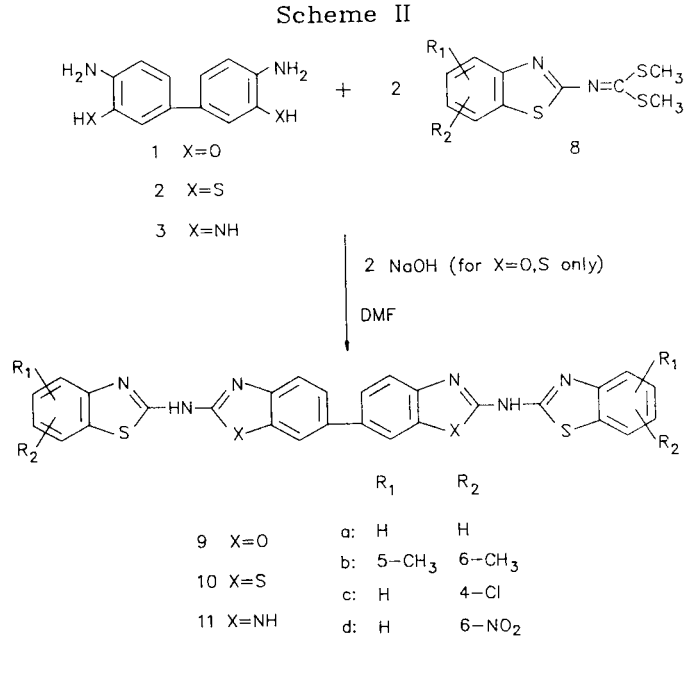
Thus, methyl *N*-aryldithiocarbamates **4** were made to react with the 3,3'-disubstituted-4,4'-diaminobiphenyls **1** [6], **2** [7] and **3**, respectively (Scheme I).

Scheme I



For **1** and **2** reactions take place in 7-8 hours in the presence of red mercury(II) oxide in refluxing dimethylformamide. It is interesting to note that, to the best of our knowledge, only one of these compounds, **6a**, had previously been prepared in low yield (18%), by the reaction of **2** with phenyl isothiocyanate under harsh conditions [8]. Again, it was found that a mixture of a methyl dithiocarbamate and red mercury(II) oxide produced better results than those obtained with the corresponding isothiocyanate (*cf.* [1]). As expected, milder conditions (60-70°, 5 hours) can be used in the synthesis of the benzimidazole derivatives **7**, though the reaction must be carried out in a nitrogen atmosphere in order to avoid darkening and tar formation. A inert atmosphere is also advisable for the preparation of **5**, but in the case of **6** produces no significant improvement (Table 1).

Scheme II



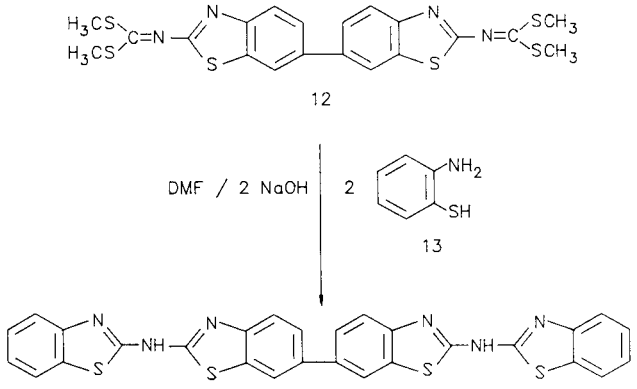
An alternative approach was used in the synthesis of the bis(2-benzothiazolylamino) derivatives **9**, **10** and **11** (Scheme II), which takes advantage of the high electrophilicity of dimethyl *N*-(2-benzothiazolyl)dithiocarbonimidates **8** [9]. The reactions of **8** with **1**, **2** and **3** were car-

ried out in refluxing dimethylformamide and afforded tetrabenzoazole derivatives **9**, **10** and **11**, respectively, in good to very good yields (Table 2).

The synthesis of **9** and **10** can only be successfully carried out in the presence of two equivalents of sodium hydroxide, which are used to generate the corresponding anions from **1** and **2**, respectively. This procedure is not necessary in the preparation of benzimidazoles **11**. As before, the preparation of **9** and **11**, but not of **10**, was carried out in a nitrogen atmosphere.

The structure of one of these compounds, **10a**, was confirmed by an independent synthesis from tetramethyl *N*,*N*'-[6,6'-bibenzothiazole-2,2'-diyl]bisdithiocarbonimidate **12** [10] and 2-aminothiophenol **13** (Scheme III).

Scheme III



On comparing Schemes I and II it is interesting to note that for the introduction of arylamino groups, dithiocarbamates are the more suitable reagents, while dithiocarbonimidates must be used for the introduction of 2-benzothiazolylamino moieties.

The lower electrophilicity of dimethyl *N*-aryldithiocarbonimidates compared to that of their benzothiazole analogues **8** accounts for the use of dithiocarbamates **4** when arylamino groups are introduced. This alternative pattern of reactivity has proved very useful in the synthesis of a wide variety of heterocyclic rings.

N-Arylsulfonyldithiocarbamic acid derivatives show behaviour which comes between the two mentioned above and which is exemplified in the synthesis of the arylsulfonyl aminobenzoazoles **16**, **17** and **18**.

Thus, compounds **14** did not react with **1**, **2** or **3**, the starting materials being recovered unchanged. This result was not completely unexpected since although **14** has been reported to give simple 2-arylsulfonylaminobenzoazoles in medium yields [5], more electrophilic reagents have had to be used in similar cases [11]. Here, the alternative approach of increasing the nucleophilicity of **1** and **2** was adopted and permitted the preparation of bibenzoxazoles and bibenzothiazoles **16** and **17**, respectively in good yields. Attempts to synthesize compounds **18** by this method were unsuccessful since **14** were converted into the corresponding arenesulfonamides. On the other hand, the use of dithiocarbamic acid esters **15** in conjunction with mercury(II) oxide allowed the synthesis of compounds **16** in good yields, as expected (Table 3).

Therefore, it can be seen that the choice of the appropriate dithiocarbamic reagent for a given transformation, depends to a considerable degree on the nature

Table 1

2,2'-Bis(arylamino)-6,6'-bibenzoazoles

Compound	mp (°C) (Recrystallization solvent)	Yield (%)
5a	>300 (DMF/H_2O)	48
5b	>300 (DMF/H_2O)	63
5c	>300 (DMF/H_2O)	60
5d	>300 (DMF/H_2O)	50
6a	>300 (DMF/H_2O)	60
6b	>300 (DMF/H_2O)	51
6c	>300 (DMF/H_2O)	67
6d	>300 (DMF/H_2O)	40
7a	>300 (EtOH/H_2O)	87
7b	>300 (MeOH/H_2O)	79
7c	>300 (MeOH/H_2O)	78
7d	>300 (MeOH/H_2O)	74

Table 2

2,2'-Bis(2-benzothiazolylamino)-6,6'-bibenzoazoles

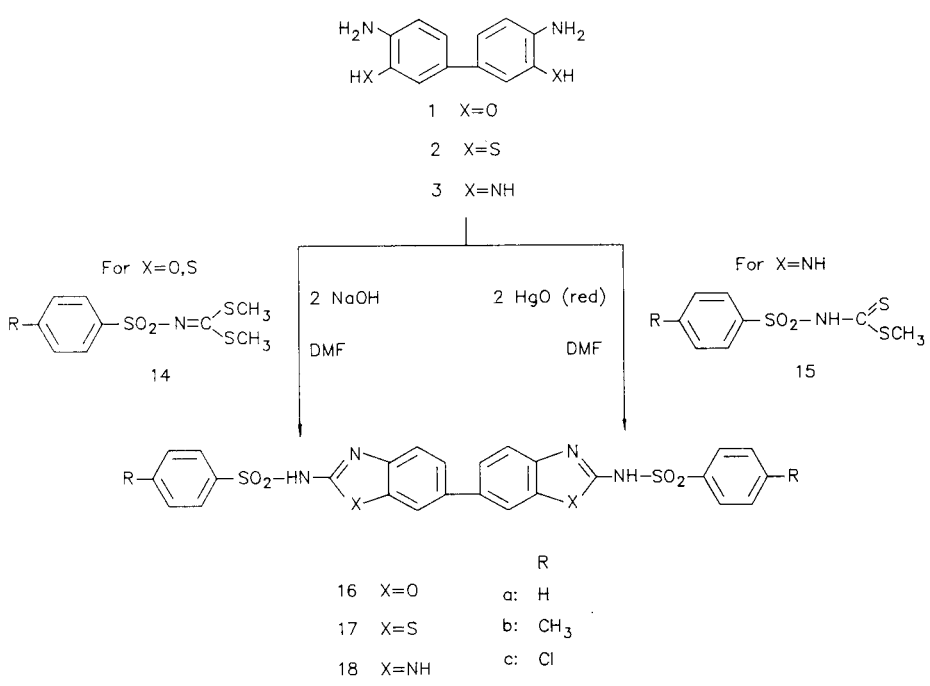
Compound	mp (°C) (Recrystallization solvent)	Yield (%)
9a	>300 (DMF)	68
9b	>300 (DMF)	58
9c	>300 (DMF)	83
9d	>300 (DMF)	75
10a	>300 (DMF/H_2O)	90
10b	>300 (DMF/H_2O)	78
10c	>300 (DMF/H_2O)	84
10d	>300 (DMF)	96
11a	>300 (DMF)	73
11b	>300 (DMF)	65
11c	>300 (DMF)	83
11d	>300 (DMF)	90

Table 3

2,2'-Bis(arylsulphonylamino)-6,6'-bibenzoazoles

Compound	mp (°C) (Recrystallization solvent)	Yield (%)
16a	>300 (DMF/H_2O)	95
16b	>300 (DMF/H_2O)	73
16c	>300 (DMF/H_2O)	73
17a	>300 (DMF/H_2O)	83
17b	>300 (DMF/H_2O)	73
17c	>300 (DMF/H_2O)	93
18a	>300 (DMF/H_2O)	92
18b	>300 (DMF/H_2O)	79
18c	>300 (DMF/H_2O)	77

Scheme IV



of the *N*-linked group which is to be introduced. A useful guideline is as follows: for 2-aminobenzothiazoles, dithiocarbonimidic acid esters are specially useful, while for aromatic amines, dithiocarbamic acid esters are generally preferred; the corresponding derivatives of arenesulfonamides show a borderline reactivity.

To sum up, the methods herein reported show great versatility since bibenzoxazoles, bibenzothiazoles and bibenzimidazoles can be prepared in medium to very good yields using readily available starting materials.

Furthermore, these one-pot methods avoid the use of the corresponding isothiocyanates, which either show very poor reactivity (phenylisothiocyanate [8]) or are unavailable (2-benzothiazolylisothiocyanate).

EXPERIMENTAL

Melting points were determined on a Büchi 510 apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer FT 1600 instrument. The nmr spectra were recorded on a Bruker WP 80 CW spectrometer with TMS as internal reference.

Synthesis of 2,2'-Bis(arylamino)-6,6'-bibenzoxazoles **5**.

General Procedure.

To a suspension of 1.0 mmole of 3,3'-dihydroxybenzidine **1** and 2.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide was added 2.0 mmoles of the corresponding methyl *N*-aryldithiocarbamate **4** in 5 ml of dimethylformamide, at room temperature. Once **4** has been added, the mixture was refluxed for 8 hours under a nitrogen atmosphere. After cooling, the mixture was filtered and to the filtrate were added 10 ml of water. The precipitate thus obtained was filtered off, washed with water, dried and recrystallized.

2,2'-Bis(phenylamino)-6,6'-bibenzoxazole (**5a**).

This compound had ir: 1670 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.6 (s, 1H), 7.8-6.7 (m, 8H).

Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.36; H, 4.34; N, 13.39. Found: C, 74.81; H, 4.37; N, 13.29.

2,2'-Bis(4-tolylamino)-6,6'-bibenzoxazole (**5b**).

This compound had ir: 1680 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.6 (s, 1H), 7.7-7.2 (m, 5H), 6.9 (d, 2H, J = 9), 2.5 (s, 3H).

Anal. Calcd. for $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55. Found: C, 75.15; H, 4.95; N, 12.59.

2,2'-Bis(4-chlorophenylamino)-6,6'-bibenzoxazole (**5c**).

This compound had ir: 1680 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.6 (s, 1H), 7.8-7.0 (m, 7H).

Anal. Calcd. for $C_{26}H_{16}Cl_2N_4O_2$: C, 64.08; H, 3.31; N, 11.50. Found: C, 63.96; H, 3.40; N, 11.54.

2,2'-Bis(4-methoxyphenylamino)-6,6'-bibenzoxazole (**5d**).

This compound had ir: 1680 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.5 (s, 1H), 7.6-7.2 (m, 5H), 6.6 (d, 2H, J = 9), 3.8 (s, 3H).

Anal. Calcd. for $C_{28}H_{22}N_4O_4$: C, 70.28; H, 4.63; N, 11.71. Found: C, 70.15; H, 4.59; N, 11.73.

Synthesis of 2,2'-Bis(arylamino)-6,6'-bibenzothiazoles **6**.

General Procedure.

These compounds were prepared in exactly the same way as compounds **5**, the only difference being that 3,3'-dimercaptobenzidine **2** was used instead of 3,3'-dihydroxybenzidine **1**.

2,2'-Bis(phenylamino)-6,6'-bibenzothiazole (**6a**).

This compound had ir: 1620 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 11.0 (s, 1H), 8.1 (s, 1H), 7.9-7.3 (m, 6H), 7.1-6.9 (m, 1H).

Anal. Calcd. for $C_{26}H_{18}N_4S_2$: C, 69.31; H, 4.03; N, 12.43. Found: C, 69.42; H, 4.19; N, 12.54.

2,2'-Bis(4-tolylamino)-6,6'-bibenzothiazole (**6b**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.0 (s, 1H), 8.1 (s, 1H), 7.8-7.6 (m, 4H), 7.2 (d, 2H, J = 8), 2.2 (s, 3H).

Anal. Calcd. for $C_{28}H_{22}N_4S_2$: C, 70.26; H, 4.63; N, 11.71. Found: C, 70.13; H, 4.61; N, 11.65.

2,2'-Bis(4-chlorophenylamino)-6,6'-bibenzothiazole (**6c**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.0 (s, 1H), 8.1 (s, 1H), 7.9-7.2 (m, 6H).

Anal. Calcd. for $C_{26}H_{16}Cl_2N_4S_2$: C, 60.12; H, 3.10; N, 10.79. Found: C, 60.12; H, 3.10; N, 10.79.

2,2'-Bis(4-methoxyphenylamino)-6,6'-bibenzothiazole (**6d**).

This compound had ir: 1620 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.0 (s, 1H), 8.1 (s, 1H), 7.8-7.0 (m, 6H), 3.6 (s, 3H).

Anal. Calcd. for $C_{28}H_{22}N_4O_2S_2$: C, 65.86; H, 4.34; N, 10.97. Found: C, 65.80; H, 4.26; N, 11.01.

Synthesis of 2,2'-Bis(arylamino)-5,5'(6,6')-bibenzimidazoles **7**.

General Procedure.

To a suspension of 1.0 mmole of 3,3'-diaminobenzidine **3** and 2.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide was added a solution of 2.0 mmoles of the appropriate methyl *N*-aryldithiocarbamate **4** in 10 ml of dimethylformamide at room temperature. The mixture was heated at 70° under a nitrogen atmosphere for 5 hours and then filtered in hot. The filtrate was poured into water (100 ml); the precipitate thus obtained was filtered off, washed with water, dried and recrystallized.

2,2'-Bis(phenylamino)-5,5'(6,6')-bibenzimidazole (**7a**).

This compound had ir: 1620 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.5 (s, 2H), 7.8-6.7 (m, 8H).

Anal. Calcd. for $C_{26}H_{20}N_6$: C, 74.98; H, 4.84; N, 20.18. Found: C, 75.08; H, 5.01; N, 20.06.

2,2'-Bis(4-tolylamino)-5,5'(6,6')-bibenzimidazole (**7b**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.4 (s, 2H), 7.8-6.9 (m, 7H), 2.3 (s, 3H).

Anal. Calcd. for $C_{28}H_{24}N_6$: C, 75.65; H, 5.44; N, 18.91. Found: C, 75.41; H, 5.62; N, 18.84.

2,2'-Bis(4-chlorophenylamino)-5,5'(6,6')-bibenzimidazole (**7c**).

This compound had ir: 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.5 (s, 2H), 7.9-6.9 (m, 7H).

Anal. Calcd. for $C_{26}H_{18}Cl_2N_6$: C, 64.34; H, 3.74; N, 17.31. Found: C, 64.31; H, 3.73; N, 17.45.

2,2'-Bis(4-methoxyphenylamino)-5,5'(6,6')-bibenzimidazole (**7d**).

This compound had ir: 1620 cm^{-1}: ^1H-nmr (DMSO-d_6): δ 9.3 (s, 2H), 7.7-7.2 (m, 5H), 6.8 (d, 2H, J = 8), 3.75 (s, 3H).

Anal. Calcd. for $C_{28}H_{24}N_6O_2$: C, 70.57; H, 5.08; N, 17.64. Found: C, 70.75; H, 4.99; N, 17.73.

Synthesis of 2,2'-Bis(2-benzothiazolylamino)-6,6'-bibenzoxazoles **9**.

General Procedure.

A solution of 1.0 mmole of 3,3'-dihydroxybenzidine in 10 ml of dimethylformamide was treated under a nitrogen atmosphere with 0.4 ml of aqueous 5 molar sodium hydroxide, and the mixture was stirred at room temperature for 30 minutes. A solution of 2.0 mmoles of the appropriate dimethyl *N*-(2-benzothiazolyl)-dithiocarbonimidate **8** was then added dropwise and the reaction mixture was heated under reflux until no more methylmercaptan was evolved (7-9 hours). After cooling, the mixture was treated with 2 ml of acetic acid. The precipitate thus obtained was filtered off, washed with water, methanol and ether, dried and recrystallized.

2,2'-Bis(2-benzothiazolylamino)-6,6'-bibenzoxazole (**9a**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr (TFA): δ 8.0-7.5 (m).

Anal. Calcd. for $C_{28}H_{16}N_6O_2S_2$: C, 63.15 H, 3.03; N, 15.78. Found: C, 63.16; H, 3.04; N, 15.70.

2,2'-Bis(5,6-dimethyl-2-benzothiazolylamino)-6,6'-bibenzoxazole (**9b**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr (TFA): δ 7.9 (s, 1H), 7.8-7.5 (m, 4H), 2.4 (s, 6H).

Anal. Calcd. for $C_{32}H_{24}N_6O_2S_2$: C, 65.29; H, 4.11; N, 14.28. Found: C, 65.19; H, 4.29; N, 14.21.

2,2'-Bis(4-chloro-2-benzothiazolylamino)-6,6'-bibenzoxazole (**9c**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (TFA): δ 7.9 (s, 1H), 7.8-7.5 (m, 5H).

Anal. Calcd. for $C_{28}H_{14}Cl_2N_6O_2S_2$: C, 55.91; H, 2.35; N, 13.97. Found: C, 55.88; H, 2.19; N, 13.87.

2,2'-Bis(6-nitro-2-benzothiazolylamino)-6,6'-bibenzoxazole (**9d**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr (TFA): δ 8.9 (s, 1H), 8.6 (d, 1H, J = 8), 8.1-7.7 (m, 4H).

Anal. Calcd. for $C_{28}H_{14}N_8O_6S_2$: C, 54.02; H, 2.27; N, 18.00. Found: C, 54.15; H, 2.39; N, 18.03.

Synthesis of 2,2'-bis(2-benzothiazolylamino)-6,6'-bibenzothiazoles **10**.

General Procedure.

The synthesis is identical to that described for compounds **9**, but with 3,3'-dimercaptobenzidine **2** as a starting material.

2,2'-Bis(2-benzothiazolylamino)-6,6'-bibenzothiazole (**10a**).

This compound had ir: 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 8.3 (s, 1H), 7.9-7.2 (m, 6H).

Anal. Calcd. for $C_{28}H_{16}N_6S_4$: C, 59.55; H, 2.86; N, 14.88. Found: C, 59.55; H, 2.99; N, 14.76.

2,2'-Bis(5,6-dimethyl-2-benzothiazolylamino)-6,6'-bibenzothiazole (**10b**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 8.2 (s, 1H), 7.9-7.5 (m, 3H), 7.2 (s, 1H), 2.3 (s, 6H).

Anal. Calcd. for $C_{32}H_{24}N_6S_4$: C, 61.91; H, 3.90; N, 13.54. Found: C, 62.06; H, 3.82; N, 13.72.

2,2'-Bis(4-chloro-2-benzothiazolyl)-6,6'-bibenzothiazole (**10c**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 8.3 (s, 1H), 7.9-7.1 (m, 5H).

Anal. Calcd. for $C_{28}H_{14}Cl_2N_6S_4$: C, 53.08; H, 2.23; N, 13.26. Found: C, 53.31; H, 2.09; N, 13.26.

2,2'-Bis(6-nitro-2-benzothiazolylamino)-6,6'-bibenzothiazole (**10d**).

This compound had ir: 1610 cm^{-1}; ^1H-nmr: insoluble in all the usual solvents.

Anal. Calcd. for $C_{28}H_{14}N_8O_4S_4$: C, 51.37; H, 2.16; N, 17.11. Found: C, 51.56; H, 2.19; N, 17.19.

Alternative Synthesis of **10a**.

Aqueous 5 *M* sodium hydroxide (0.4 ml, 2.0 mmoles) was added to a solution of 2-aminothiophenol **13** (2.0 mmoles) in dimethylformamide (10 ml) and the mixture was stirred at room temperature for 30 minutes. A solution of **12** (1.0 mmole) [10] in DMF (10 ml) was then added and the mixture was refluxed until evolution of methanethiol ceases (*ca.* 7 hours). After cooling, the mixture was neutralized with a few drops of acetic acid to precipitate the desired azole, which was filtered off, washed with ethanol and recrystallized.

Synthesis of 2,2'-Bis(2-benzothiazolylamino)-5,5'(6,6')-bibenzimidazoles **11**.

General Procedure.

A solution of 1.0 mmole of 3,3'-diaminobenzidine **3** and 2.0 mmoles of the corresponding dimethyl *N*-(2-benzothiazolyl)dithiocarbonimidate **8** in 10 ml of dimethylformamide was heated under reflux in a nitrogen atmosphere until no more methylmercaptan was evolved (14-16 hours). After cooling, the mixture was poured into methanol (20 ml), and the precipitate thus obtained was filtered off, washed with methanol and ether, dried and recrystallized.

2,2'-Bis(2-benzothiazolylamino)-5,5'(6,6')bibenzimidazole (**11a**).

This compound had ir: 1640 cm^{-1}; ^{1}H-nmr (TFA): δ: 7.9-7.5 (m).

Anal. Calcd. for $C_{28}H_{18}N_8S_2$: C, 63.38; H, 3.42; N, 21.12. Found: C, 63.39; H, 3.59; N, 21.30.

2,2'-Bis(5,6-dimethyl-2-benzothiazolylamino)-5,5'(6,6')-bibenzimidazole (**11b**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (TFA): δ 8.0-7.5 (m, 5H), 2.3 (s, 6H).

Anal. Calcd. for $C_{32}H_{26}N_8S_2$: C, 65.51; H, 4.47; N, 19.10. Found: C, 65.55; H, 4.46; N, 19.04.

2,2'-Bis(4-chloro-2-benzothiazolylamino)-5,5'(6,6')-bibenzimidazole (**11c**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr: insoluble in all the usual solvents.

Anal. Calcd. for $C_{28}H_{16}Cl_2N_8S_2$: C, 56.10; H, 2.69; N, 18.69. Found: C, 56.17; H, 2.87; N, 18.84.

2,2'-Bis(6-nitro-2-benzothiazolylamino)-5,5'(6,6')-bibenzimidazole (**11d**).

This compound had ir: 1625 cm^{-1}; ^{1}H-nmr: insoluble in all the usual solvents.

Anal. Calcd. for $C_{28}H_{16}N_{10}O_4S_2$: C, 54.19; H, 2.60; N, 22.57. Found: C, 53.99; H, 2.56; N, 22.48.

Synthesis of 2,2'-bis(arylsulphonylamino)-6,6'-bibenzoxazoles **16**.

General Procedure.

The synthesis is identical to that described for compounds **9** but dimethyl *N*-(arylsulphonyl)dithiocarbonimidates **14** were used instead of **8** as starting material.

2,2'-Bis(phenylsulphonylamino)-6,6'-bibenzoxazole (**16a**).

This compound had ir: 1650 cm^{-1}; ^{1}H-nmr (TFA): δ 8.0 (d, 2H, J = 8), 7.7-7.5 (m, 6H).

Anal. Calcd. for $C_{26}H_{18}N_4O_6S_2$: C, 57.14; H, 3.32; N, 10.25. Found: C, 57.15; H, 3.27; N, 10.20.

2,2'-Bis(tosylamino)-6,6'-bibenzoxazole (**16b**).

This compound had ir: 1640 cm^{-1}; ^{1}H-nmr (TFA): δ 8.0 (d, 2H, J = 8), 7.8-7.3 (m, 5H), 2.5 (s, 3H).

Anal. Calcd. for $C_{28}H_{22}N_4O_6S_2$: C, 58.53; H, 3.86; N, 9.75. Found: C, 58.74; H, 3.77; N, 9.87.

2,2'-Bis(4-chlorophenylsulphonylamino)-6,6'-bibenzoxazole (**16c**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (TFA): δ 8.0 (d, 2H, J = 9), 7.7-7.3 (m, 5H).

Anal. Calcd. for $C_{26}H_{16}Cl_2N_4O_6S_2$: C, 50.74; H, 2.62; N, 9.10. Found: C, 50.95; H, 2.58; N, 9.27.

Synthesis of 2,2'-Bis(arylsulphonylamino)-6,6'-bibenzothiazoles **17**.

General Procedure.

These compounds were prepared in exactly the same way as compounds **9**, the only difference being that **2** replaced **1** and **14** was used instead of **9** as starting materials.

2,2'-Bis(phenylsulphonylamino)-6,6'-bibenzothiazole (**17a**).

This compound had ir: 1660 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.2 (s, 1H), 8.0-7.3 (m, 7H).

Anal. Calcd for $C_{26}H_{18}N_4O_4S_4$: C, 53.96; H, 3.14; N, 9.68. Found: C, 53.78; H, 3.06; N, 9.76.

2,2'-Bis(tosylamino)-6,6'-bibenzothiazole (**17b**).

This compound had ir: 1660 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.2 (s, 1H), 8.0-7.2 (m, 6H), 2.3 (s, 3H).

Anal. Calcd for $C_{28}H_{22}N_4O_4S_4$: C, 55.43; H, 3.65; N, 9.23. Found: C, 55.54; H, 3.53; N, 9.36.

2,2'-Bis(4-chlorophenylsulphonylamino)-6,6'-bibenzothiazole (**17c**).

This compound had ir: 1660 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 8.2 (s, 1H), 8.0-7.2 (m, 6H).

Anal. Calcd. for $C_{26}H_{16}Cl_2N_4O_4S_4$: C, 48.22; H, 2.49; N, 8.65. Found: C, 48.09; H, 2.40; N, 8.70.

Synthesis of 2,2'-Bis(arylsulphonylamino)-5,5'(6,6')-bibenzimidazoles **18**.

General Procedure.

To a suspension of 1.0 mmole of 3,3'-diaminobenzidine **3** and 2.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide were added 2.0 mmoles of the corresponding methyl *N*-(arylsulphonyl)dithiocarbamate **15** in 5 ml of dimethylformamide, and the mixture was stirred at room temperature for 3 hours. Subsequent work-up was identical to that described for compounds **5**.

2,2'-Bis(phenylsulphonylamino)-5,5'(6,6')-bibenzimidazole (**18a**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 12.0 (s, 2H), 7.7 (d, 2H, J = 8), 7.4-7.0 (m, 6H).

Anal. Calcd. for $C_{26}H_{20}N_6O_4S_2$: C, 57.34; H, 3.70; N, 15.43. Found: C, 57.23; H, 3.53; N, 15.37.

2,2'-Bis(tosylamino)-5,5'(6,6')-bibenzimidazole (**18b**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 12.0 (s, 2H), 7.8 (d, 2H, J = 8), 7.4-7.0 (m, 5H), 2.6 (s, 3H).

Anal. Calcd. for $C_{28}H_{24}N_6O_4S_2$: C, 58.73; H, 4.22; N, 14.68. Found: C, 58.52; H, 4.16; N, 14.50.

2,2'-Bis(4-chlorophenylsulphonylamino)-5,5'(6,6')-bibenzimidazole (**18c**).

This compound had ir: 1625 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 12.0 (s, 2H), 8.0 (d, 2H, J = 8), 7.6-7.2 (m, 5H).

Anal. Calcd. for $C_{26}H_{18}Cl_2N_6O_4S_2$: C, 50.90; H, 2.96; N, 13.70. Found: C, 51.01; H, 3.01; N, 13.83.

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